

ATMOSPHERIC CARBON: THE IMPORTANCE OF ACCELERATOR MASS SPECTROMETRY *

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Knowledge of the sources, transport and sinks for carbonaceous gases and particles in the atmosphere is of great concern both for understanding the carbon cycle and for assessing man's influence on atmospheric visibility, health effects and climate. Carbon isotopes (notably ^{14}C) are quite important in tracing such species and in validating models based on emissions inventories, dispersion algorithms, and trace inorganic or organic mass balance. Accelerator mass spectrometry (AMS) offers considerable promise to this field, for useful sample size may be decreased by three orders of magnitude, resulting in greatly improved spatial, temporal and chemical resolution. Special problems which have been addressed with the use of ^{14}C -AMS are reviewed, including the study of sources of elemental, organic (particulate), and gaseous carbon compounds in the atmosphere. This report concludes with a brief review of techniques which have been used for 10–100 μg carbon samples, and a discussion of special atmospheric (urban particulate) Standard Reference Materials.

1. Introduction

The atmosphere serves as a reservoir and conducting medium for a myriad of carbon compounds, ranging from the simplest of gases (CO_2 – the end product of all combustion) to complex polynuclear and polymeric structures comprising the bulk of carbonaceous particles. Many of these species have undesirable effects on climate, visibility, and health; and increasing portions are believed generated through the activities of man [1–3]. The potential impacts of many of the trace carbonaceous gases and particles often outweigh their relative concentrations, as seen in table 1. This table is presented to indicate the nature, effects, and concentrations of a few of the more significant atmospheric

species. The values in brackets indicate the concentrations considered dangerous (air quality standard – US). These species range from mostly natural (CH_4) to largely man-made (halocarbons, $^{13}\text{CD}_4$). (This last compound, which has been used as a megameter tracer for air masses, is included both as a possible challenge for future AMS and to indicate the extremum in the range of atmospheric concentrations [4,5].)

Radiocarbon (^{14}C) has proved quite useful in distinguishing sources for many of the carbonaceous gases and particles, due to its unique power to discriminate fossil from contemporary (biogenic) carbon [6]. AMS offers great promise for the advancement of such studies, both for the measurement of ^{14}C in many of the rarer (but still very significant) carbonaceous species

Table 1
Atmospheric carbon

Species	Concentration (mg C/m ³ air)	Effects
CO_2	180. ¹	Greenhouse
CH_4	0.80 ± 0.05	Greenhouse
CO	0.06 to 20. [17]	– OH; toxic
Hydrocarbons	$< 10^{-3}$ to 2. [0.14]	+ Tropospheric O_3
Halocarbons	10^{-5} to 10^{-3}	Stratospheric O_3
Particles	$< 10^{-3}$ to 0.1 [0.075]	Visibility + ...
Elemental-C	≤ 0.05	Atmospheric Heating
Polycyclic (PAH)	$\leq 10^{-4}$ [10^{-3}]	Mutagenic + ...
...
$^{13}\text{CD}_4$	$\sim 10^{-17}$	Tracer (Mm)

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and for the assay of individual chemical fractions. Taking a reasonable sample size as 100 m³ air and a potential AMS capability of 10 µg carbon, we see that AMS may make possible the measurement of nearly all the species listed in table 1.

1.1. Some unresolved issues: nature and importance

Critical issues in the study of atmospheric carbon (excepting CO, CO₂) are collected in table 2. Volatile organic emissions are dominated by Nature on a global scale, but there are significant disagreements as to whether high local or regional ozone concentrations result primarily from naturally emitted olefins (terpenes, isoprene), or from fossil hydrocarbons generated by man [3]. A dramatic change in the substitution of wood for fossil fuel (gas, petroleum) has occurred in the past few years, and ¹⁴C has become the accepted direct (natural) tracer for wood-burning carbon [7]. Local burning of wood has resulted in a number of scientific investigations and legal-institutional actions in regions having meteorological inversions and heavy winter-time fireplace (or woodstove) use, such as ski valleys and northern towns [8,9].

Polycyclic aromatic hydrocarbons (PAH), soot and polymeric carbon are products of incomplete combustion. Their relative abundances and structure reflect the fuel and combustion conditions (vide infra), and partly as a result, relatively low temperature, fuel-rich wood burning is considered the major source of PAH in the US [10]. Some indication of the rising importance of these forms of atmospheric carbon is given in fig. 1, which shows (a) the more than ten-fold increase in PAH

during this century [11], and (b) the major contribution of diesel vehicles to the soot (or "elemental [amorphous carbon]") in Los Angeles despite the fact that they constitute but a small fraction of the mobile source population [12]. Increase in PAH, especially the strong carcinogen BaP, is of some concern because of mutagenic and carcinogenic effects which may well outstrip man's ability to adapt. Atmospheric methane is increasing globally [13], yet major uncertainties remain concerning its sources. Since methane is one of the significant "greenhouse gases", its source apportionment and source forecasting are crucial for our projections of world climate and interpretation of the role of CO₂ [1].

2. Sources; molecular and isotopic tracers

Sources of carbonaceous species and potential tracing techniques are listed in table 3. Broadly speaking we may categorize organic species as originating from direct emissions or from combustion. Identification and apportioning ("tracing") of sources is most effectively accomplished with unique and robust (unchanging) isotopic or molecular markers whose composition and abundance give a direct measure of the relative source contributions to the ambient atmospheric carbon compounds of concern. ¹⁴C is one of the most reliable soot tracers, but its discrimination power is much enhanced when it is used in combination with other isotopic or chemical tracers, as indicated in fig. 2 [14]. Biosphere emissions and certain of their pyrolysis products are often marked by unique structural features which aid in

Table 2
Some observations and critical issues

Volatile organic carbon [VOC]

- Globally, anthropogenic emissions: 5–20% of the total
- Discrepancies (emission/concentration) re: O₃ precursors (terpenes, isoprene)

Wood burning

- Return to ancient fuel → health, institutional, source-tracing problems
- Largest source of PAH in US (est.); increased seasonal pollution alerts (CO, aerosols)

PAH and soot [C_e]

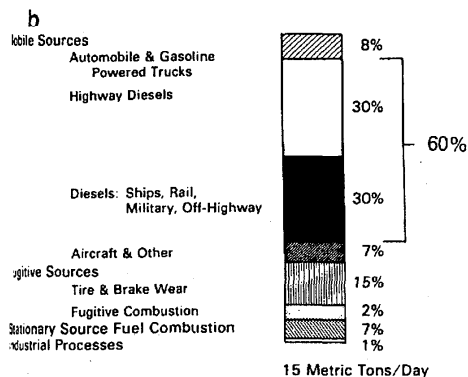
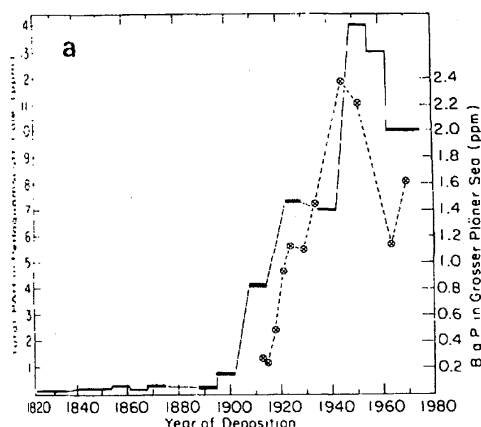
- Formed in all pyrolysis, fuel-rich combustion; health and climatic effects
- Tenfold mutagen (PAH) increase this century; tenfold Arctic seasonal effect (C_e)
- Structure reflects source and combustion conditions (temperature, ...)

Methane

- Significant global increase, but source uncertainties (termites); greenhouse effect

Accelerator mass spectrometry

- Major promise for µ-¹⁴C-chemistry → origins of atmospheric carbon



[Diesels (1980) Account for < 5% of Fuel Consumption]

Fig. 1. Combustion carbon (PAH, soot) from man's activities. Part (a) [top] shows the growth of PAH as found in Petquamscutt River sediment (solid curve, left scale) and of benzo(a)pyrene (BaP) in the Gosser Ploner Sea (dotted, right scale) (ref. [11]). Part (b) [bottom] indicates the major contribution of diesel vehicles to soot (elemental carbon particles) in Los Angeles, based on an emissions inventory (ref. [12]).

qualitative identification. One example is retene, an alkylated phenanthrene, which results from pyrolysis of the abietic acid found in softwoods [9]. Another example is given in fig. 3 where we show the odd/even paraffin carbon-number preference, characteristic of biogenic material [15], superposed on the hydrocarbon "hump" which characterizes the complex mixture of petroleum hydrocarbons. The aerosol sample in question was obtained in the Los Angeles suburbs, and ^{14}C analysis indicated that roughly half the carbon was biogenic [6].

Table 3
Sources of atmospheric carbon

Emissions	
Biosphere – CH_4 , VOC, paraffins (odd/even), fatty acids (even/odd) Geosphere (seeps) – CH_4 , ..., complex C_{10} – C_{30} hydrocarbons ("hump")	
Pyrolysis/combustion	
Wild fires	Retene, (K), CH_3Cl
Residential wood	
Fossil fuel	CO , VOC, pyrolysate, PAH, soot
Geopyrolysis	
	Graphite, + ...
Tracing	
Modeling (emission, dispersion, reaction)	
Unique tracers (chemical, isotopic)	
Composition, structure ("fingerprints")	
Multivariate analysis	

Pyrolytic PAH and soot (and polymeric carbon) are generally robust, carry structural (tracer) information about their formation, and have important ecological consequences (table 1). We are therefore giving these substances special emphasis in our continuing ^{14}C chemical studies. A model of the formation process is suggested in fig. 4, indicating the most noxious of the PAH, BaP (structure VII). Patterns among the PAH formed have been shown to depend upon the combustion temperature, with lower temperatures favoring linear arrays of aromatic rings and alkyl side chains [18].

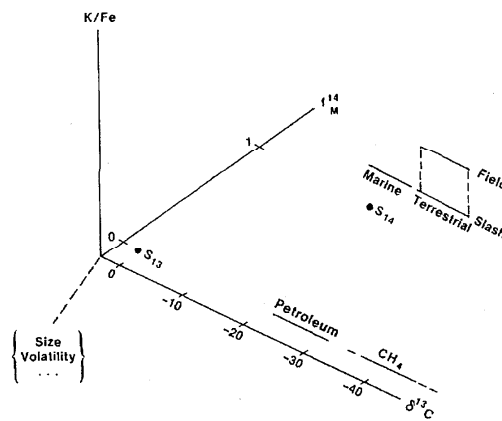


Fig. 2. Combined use of chemical and isotopic dimensions for aerosol source apportionment. ^{13}C ($\delta^{13}\text{C}$) and ^{14}C ($f_M^{14} = \text{fraction modern}$) plus the element ratio (K/Fe) discriminate among several carbon sources. Field and slash refer to vegetative burning (grass and timber clearing). S_{13} and S_{14} indicate the locations of ^{13}C (Pee Dee Belemnite) and ^{14}C (0.95 * NBS oxalic acid SRM 4990B) standards, resp.

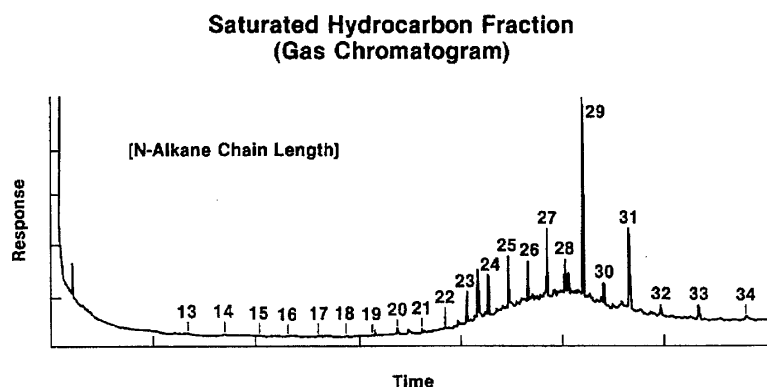


Fig. 3. Gas chromatogram of Los Angeles aerosol sample showing the fossil hydrocarbon "hump" and the odd/even pattern of the biogenic hydrocarbons [6].

The polymeric composition of the aerosol offers a more reliable indicator for the source material, as shown in our pyrolysis mass spectrometry (PyMS) studies of (a) ambient aerosol and (b) particles from the combustion of polymeric fuels (including natural polymers, as wood). Fig. 5 shows two of the pyrograms and the resultant non-linear maps (NLM) which successfully distinguished a number of carbonaceous fuels. As noted in the caption, the NLM (part b) is a convenient device for representing the differences among spectra, using a (non-linear) 2-dimensional projection of the multidimensional points - where each point comes from the multidimensional representation of the corresponding mass spectrum (part a). (The NLM is simply the multidimensional projection analogue of the more familiar mass or element ratio plot which is a planar projection of the 3-dimensional information commonly encountered in geochronology and environmental chemistry.) Fig. 6 shows a similar analysis of an eastern Utah

aerosol sample for biogenic and fossil emissions contributions, here combining isotopic (^{14}C) and structural (PyMS) analyses. The combined data proved self-consistent and indicated that about two-thirds of the ambient aerosol carbon came from the vegetative (pine, sage) sources [19].

The combination of ^{14}C and chemical/structure analysis has two extremely important consequences: (a) control or validation of the (source) model comes about through the use of methods based on quite different assumptions; and (b) independent measures lead to improved resolution and source-estimate precision. Another illustration of this powerful combination, made possible in part by the great sensitivity of AMS, is given in our recent study of vegetative and fossil emissions in which we combined the microanalytical techniques of thermogravimetric analysis (TGA), pyrolysis-gas chromatography-mass spectrometry (PyGCMS), and ^{14}C measurement of carbonaceous aerosols [20]. Some re-

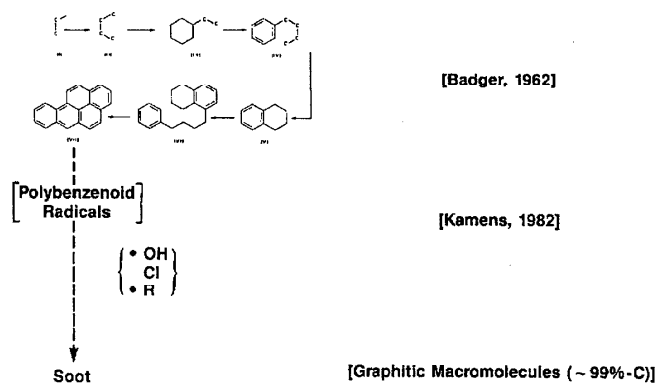


Fig. 4. Schematic representation of the pyrolytic formation of PAH (here, benzo(a)pyrene) and soot [16,17].

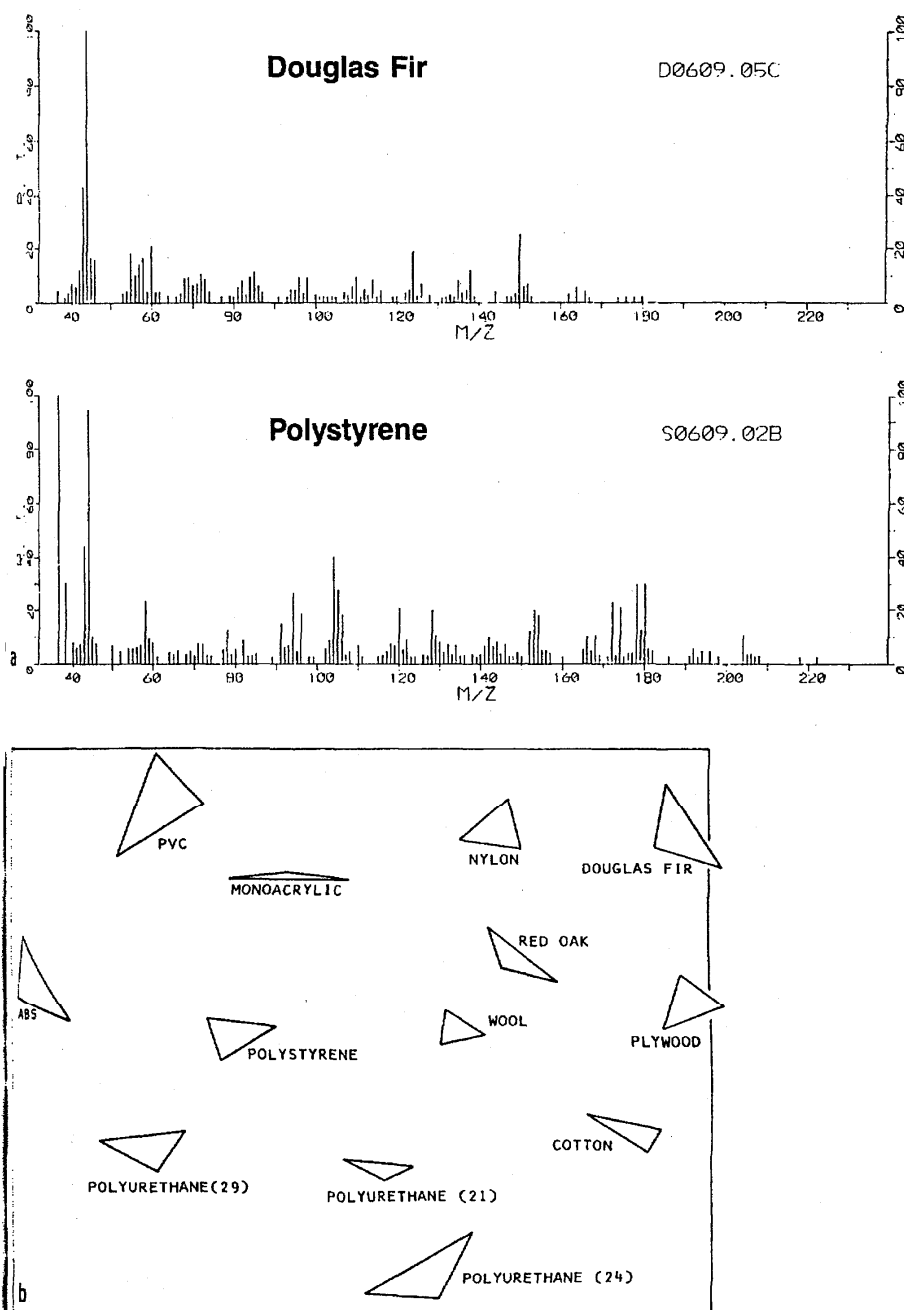


Fig. 5. Discrimination of polymer combustion aerosols with pyrolysis mass spectrometry (PyMS). Part (a) [top] shows the pyrograms for natural (Douglas fir) and synthetic (polystyrene) polymers (relative intensity vs mass). In part (b) [bottom] the resulting NLMs for combustion aerosols from several natural and synthetic polymers are given, the NLM is a distorted (non-linear) projection which tends to preserve the actual multidimensional separation of the mass pyrograms. [Each of the projected points represents a pyrolysis mass spectrum having some 200 individual dimensions (mass numbers).]

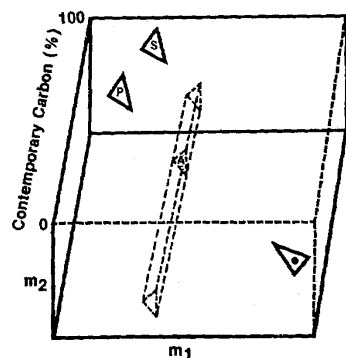


Fig. 6. Pseudo 3-dimensional map of ambient and source aerosols, combining mass pyrogram NLM with ^{14}C measurement. m_1 and m_2 are non-linear mass combinations from observed mass spectra, where: the bottom (fossil) plane (●) shows triplicate results for oil shale source aerosol; the top (contemporary) plane shows triplicate results for pine (P) and sage (S) aerosols, and the mid-plane (A) indicates the location for the ambient aerosol combined (^{14}C -PyMS) data.

sults are given in table 4, where it is seen that the more intense natural fire plume gave carbon particles which were essentially all biogenic, whereas the roadway tunnel gave completely fossil carbon particles. Not shown are the results of TGA, which indicated that the tunnel particles consisted of 53% elemental carbon (soot). (This is quite high compared to typical urban ratios [$\sim 20\%$] and the pine and sage forest fires [14–16%].) One interesting fact, which came from the molecular data (PyGCMS), was that a significant portion of the fine particulate carbon arose from roadway degradation of the styrene-butadiene copolymer in tire material.

3. Advanced ^{14}C techniques; summary of atmospheric results

The applicability of atmospheric ^{14}C as a tracer for man's use of fossil fuel was first seen in atmospheric CO_2 as the "Suess effect" [21]. The first applications to the much lower abundance carbonaceous particles came in 1955 [22] and 1960 [23] using massive atmospheric sampling and conventional gas and liquid scintillation counting techniques (see table 5). The next advance was made using miniature gas counters to assay as little as mg carbon [14,20]. Most recently, AMS has permitted us to work down to the 10–100 μg range.

Highlights of our latest AMS studies are given in table 5. The first collaborative experiment, with the University of Rochester, was designed to test the final measurement phase – viz., to determine the smallest atmospheric (carbon) sample which could be used successfully in the accelerator ion source [24]. This was found to be $\sim 20\text{--}30\ \mu\text{g}$ using direct and graphite dilution techniques. A result on the new radiocarbon dating standard (SRM 4990C), having 3% Poisson precision, was obtained with the consumption of just 8 μg carbon from a 37 μg target. An ancillary study included the first use of electromagnetic isotope separation-implantation to prepare an AMS source from CO_2 , where the implantation of the $^{14}\text{C}^{16}\text{O}^+$ beam led to an isotopic enrichment of ~ 500 .

The second AMS experiment, in collaboration with the University of Arizona, was designed to test the limits of the overall measurement process – from sample combustion to AMS ion beam counting [25]. As anticipated, this process was much more difficult, due to contamination and losses accompanying the chemical processing, so that reliable measurements currently require at least 50–100 μg carbon. The principal lim-

Table 4
Aerosol sources – ^{14}C characterization of the polymeric fraction

Source	Aerosol concentration ($\mu\text{g}/\text{m}^3$)	Extractable (%)	Contemporary carbon ^{a)} (ICM; %)
Sage environment/ (Great Divide, CO)	20	27	–
Pine environment/ (Parkview Mtn, CO)	> 16	53	73 ± 5
Sage-Aspen Fire (Leadville, CO)	2500	> 75	82 ± 5 (coarse)
Pine fire (Leadville, CO)	> 12000	> 75	105 ± 6
Vehicular emissions (Eisenhower Tunnel, CO)	2100	30	4 ± 2
Power plant emissions (Huntington, Utah)	15	> 75	-1 ± 2 (coarse)

^{a)} ICM = insoluble carbonaceous material. All ^{14}C results apply to the fine fraction ($< 0.6\ \mu\text{m}$) except where marked "coarse". Uncertainties shown are standard deviations.

Table 5
Atmospheric particles: advances in ^{14}C measurement

Conventional counters [RSD ~ 1%] ^{a)}	[Urban: median]
Clayton, Arnold, Patty (1955)	~ 6 g carbon [26% contemporary]
Lodge, Bien, Suess (1960)	~ 3.8 g carbon [14% contemporary]
Uni-Gas Counters [RSD ~ 5%] ^{a)}	
NBS (≥ 1977)	~ 5–10 mg carbon [32% contemporary]
Tandem AMS [RSD $\leq 6\%$] ^{a)}	
NBS + U. Rochester (Elmore, Gove; 1979)	~ 25 μg carbon
Evaluated μg -level, final sample vs preparation; including graphite dilution, E-M isotope enrichment-implantation	
NBS + U. Arizona (Donahue, Jull, Zabel; 1982-83)	~ 100 μg carbon
Evaluated μg level, initial sample vs preparation; including blank (~ 15 μg)+individual fractions of atmospheric particles	

^{a)} RSD denotes the relative standard deviation.

ation is the blank, which we found equivalent to ~ 15 μg of contemporary carbon. Unless this blank can be substantially reduced, it may be more profitable for the smallest of samples (~ 10 μg) to employ a direct mounting or graphite dilution technique when the initial sample is in an appropriate chemical form (e.g., atmospheric soot particles).

A summary of our atmospheric ^{14}C results is given in table 6, which contains medians (% contemporary carbon) for each molecular or regional category. In many cases (methane, Arctic Haze, rural particles) little variation was observed beyond the Poisson counting error (5–10%, relative). For urban samples, however, significant trends were noted, depending on anthropogenic and meteorological activity [6]. General observations which follow from the table are that atmospheric methane (in the region sampled) is primarily biogenic, as is the carbon in particles from the forests and desert sampled; that wood burning can have quite a significant

impact on urban particles; but that in the absence of wood (or biomass) burning, urban particulate carbon is mostly fossil – as is the carbon in the “Arctic Haze” [26].

This last result (from Point Barrow, Alaska) is especially significant, for measurements of chemical composition [27] and graphitic (soot) content [26] together with trajectory analysis, have implicated fossil fuel combustion in Central Europe and Northern Asia as sources for the seasonal incursion of urban-type particles in the Arctic. The ^{14}C results, however, are the first direct indication of a mostly fossil carbon content. The qualitative significance of the black particles, in terms of atmospheric heating, is obvious. Semi-quantitative modeling efforts suggest that “the present springtime concentrations of graphitic particles could increase the atmospheric heating rate by an amount comparable to that expected from a doubling of the CO_2 concentration” [28].

Space does not permit detailed discussion of the several categories of results, but brief amplification of the Elverum (Norway) study is in order. As noted in the table, this study was undertaken because the use of wood as a regular supplemental fuel in the suburban Oslo community was believed responsible for rather serious carbonaceous particle pollution [9]. The ^{14}C measurements were consistent with that presumption, but the results of the investigation provided much more information, because extensive organic, inorganic and meteorological data were simultaneously obtained. An especially interesting outcome of a substantial multivariate analysis was that ^{14}C was highly correlated with PAH and the softwood pyrolysis product, retene, but only moderately correlated with the presumed wood combustion tracer, potassium. A more detailed examination of the 3-dimensional pattern of variability: C, ^{14}C , K in the particles revealed a two-component potassium source. Thus, we have an interesting illustration of the power of the isotopic tracer when combined

Table 6
Ambient samples (^{14}C)

Sample	Location	Contemporary C (%) [Median]
CH_4	Eastern US	82 [CH ₄ budget]
CO	Las Vegas	– [wood burning]
Particles	Denver	29 [“brown cloud”]
	Salt Lake City	28
Urban)	Houston	34
	Los Angeles	38
	Portland	77 [vegetative burning]
	Elverum	69 [wood burning]
Rural)	Desert – Utah	88
	Forest – US	92
	Forest – USSR	80
Remote)	Point Barrow	27 [“Arctic haze”]

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